PFAS 101

Regional Science Council – Science Academy

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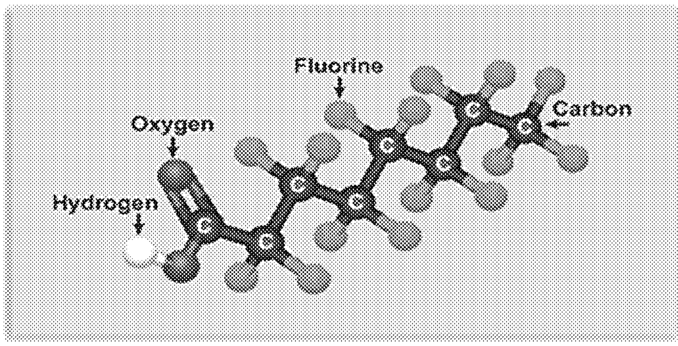


PFOA (credit – NIEHS)

PFAS Overview

- Chemistry
- Characteristics and Usage
- Fate and Transport
- Toxicology
  - Human health
  - Ecological
- Drinking Water Issues
  - Sampling and laboratory methods
  - Treatment Options
- Questions and Discussion
- Resources

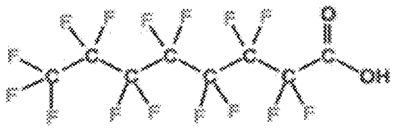
Per- and Polyfluoroalkyl Substances (PFAS)

- Prevalent
  - More than 5,000 synthetic fluorinated organic chemicals
  - Used for many years as surfactants to repel dirt, oil and water

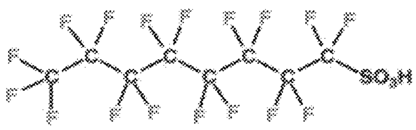
- C-F bond one of the strongest in nature
  - Persistent and Mobile
    - Bio accumulative and potentially wide range of adverse human health effects
    - Resistant to chemical/biochemical reactions
    - Soluble and mobile in water at low concentrations

Perfluoroalkyl Acids (PFAAs)

Carboxylic Acids and Carboxylates (PFCAs) and Perfluoroalkane Sulfonic Acids and Sulfonates (PFSAs)



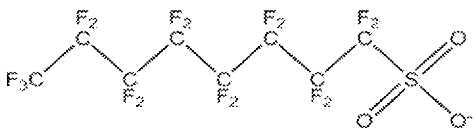
PFOA - perfluorooctanoic acid



PFOS - perfluorooctanesulfonic acid

Perfluoroalkyl Acids

PFAAs
PFSAs (sulfonates)
PFCAs (carboxylates)

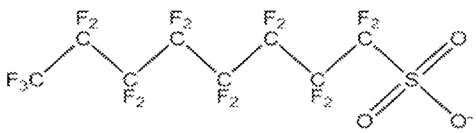


PFOS

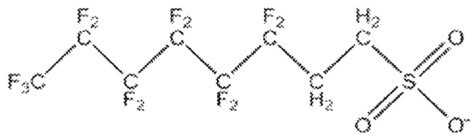
- CF ‘tail’: hydrophobic
  - Longer is more hydrophobic
  - Longer transports slower
- Functional group ‘head’
  - Water soluble
  - PFCAs transport faster than same length C chain PFSAs
- Few engineered or environmental processes degrade PFAAs

Per- vs. Poly- fluoroalkyl Substances

Perfluoroalkyl sulfonate (PFSA)



Polyfluoroalkyl Substance



PFCs ≠ PFAS

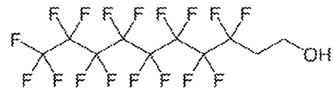
What is a Precursor?

- Polyfluoroalkyl substances that can undergo transformation to form perfluoroalkyl acids

- Mechanisms include
  - hydrolysis, photolysis and oxidation (air exposure and oxidative remediation for other chemicals may convert precursors to PFAAs over time or during treatment)
  - aerobic biologically mediated

- End products include PFOA and PFOS

- Example: 8:2 Fluorotelomer alcohol
  - Degrades environmentally to PFOA



Manufacturing History of Some PFAS

PFAS[1]	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2])
PFOA		Initial Production	Protective Coatings					
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

Notes:

1. This table includes fluoropolymers, PFAAs, and fluorotelomers. PTFE (polytetrafluoroethylene) is a fluoropolymer. PFOS, PFOA, and PFNA (perfluorononanoic acid) are PFAAs.
2. Refer to Section 3.4.
3. The dominant manufacturing process is shown in the table; note, however, that ECF and fluorotelomerization have both been, and continue to be, used for the production of select PFAS.

Sources: Prevedouros et al. 2006; Concawe 2016; Chemours 2017; Gore-Tex 2017; US Naval Research Academy 2017

ITRC, November, 2017

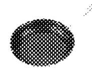
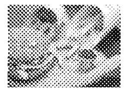
Characteristics of PFAS

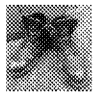
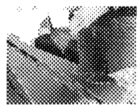
- Performance
  - Water and Oil resistant -> Lower surface tension of water
  - Powerful wetting agents
  - Chemically stable to heat, strong acids, oxidizing and reducing agents and concentrated alkalis and biodegradation
- Effects
  - Improved wetting, spreading, foam generation
  - Reduced water spotting; smaller gas bubbles and droplets
  - Enhanced liquid penetration
  - Stability

Types of Consumer Products Using Coating to Repel Water, Oil and Stains

- Textiles and Leather
  - Protective clothing, carpets, upholstery; porous concrete, grout, tile, etc. surfaces
- Paper Products
  - Cardboard, Carbonless forms, pizza boxes, fast food wrappers, microwave popcorn bags
- Personal Products

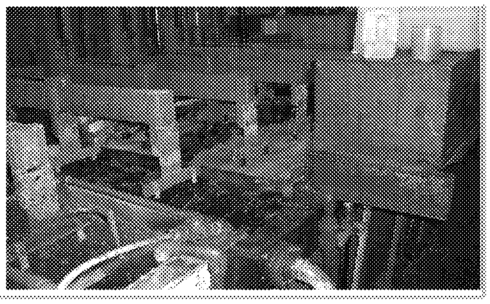



Industrial Usage

- Surfactant, corrosion prevention, mechanical wear reduction
  - Paints and Cleaners; Metal Plating and Etching
    - Mist suppressant for Cr, Cu, Ni and Sn electroplating; electroless plating of Cu and Ni-B



  - Photolithography, Semiconductor Industry
    - Anti-reflective coatings, etchants

PFAS Usage (cont'd)

- Manufacturing of plastics and fluoropolymers, resins
  - Emulsion polymerization aids; used in coatings
  - Industrial surfactants, resins, molds and plastics
- Coating and insulation
  - Wire manufacturing; non-stick cooking surfaces
- Dispersant, surface tension lowering and wetting agent
  - Lubricating greases, herbicides and insecticides
  - Floor cleaners and polishers (removes and prevents soil adhesion); coating of porous concrete, grout, tile, etc. surfaces

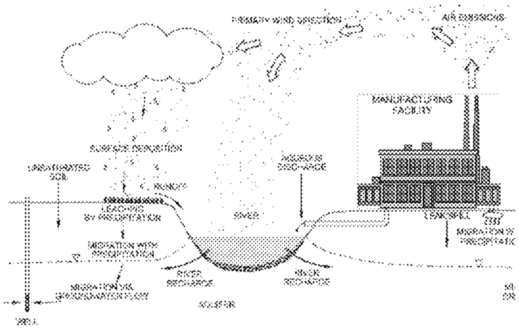
Firefighting Foams

- Formulated to
  - float on flammable liquids
  - form vapor barrier
  - cool to prevent reignition
- Aqueous Film Forming Foam (AFFF)
  - Fluorinated surfactants lower surface tension of water and form film on fuel
- Mix foam concentrate with water to make foam
- Foam solution is aerated at nozzle
- Thousands of gallons may be applied per event

EPA United States Environmental Protection Agency

Fate and Transport of PFAS

- Chemistry is COMPLEX!
- Fate
  - Abiotic and biotic transformation of precursors
- Transport
  - Moves with groundwater, into/out of surface water
  - Deposits on and leaches from soils/sediments
  - Can move in air by volatility, particulate dispersion, wind carried foam, stack emissions



Understanding PFAS Fate and Transport NEWMOA 2016

PFAS Contributors and Contamination Routes

- Industrial
  - Manufacturing
  - Use in products; mist suppression in plating facilities
    - Wastewater, including discharge to surface water; air deposition
- AFFF
  - FTAs, equipment test areas, crash/fire sites, storage areas
  - Fuel farms or other needed fire retardant systems
    - Soil, groundwater, wastewater, surface water, air movement/deposition
- Landfill leachate; Wastewater Treatment Plants
    - Groundwater, surface water, wastewater
- Biosolids land application
    - Soil, groundwater

PFAS Transport

Mobility is Complex!

- Shorter chain lengths usually faster than long chain lengths
- Carboxylates move faster than sulfonates
- Influencing Factors:
  - Ionic or neutral state (anions > zwitterions > cations (latter can remain in source area))
  - pH (more acidic increases retardation)
  - TOC (but do not fit traditional Koc-based sorption isotherm)
  - Presence of polyvalent cations (e.g., Ca+2)
  - Iron oxides (increase retardation)
  - Ionic strength (greater concentration of ions increases retardation; e.g., near salt water)
  - Remediation such as chemical oxidation alters transport with geochemistry changes (pH or cations) and can transform precursors to PFAAs

Status of PFAS

- 2000: 3M voluntary phase out of perfluorooctanyl chemistries (e.g., PFOS, PFHxS, PFOA) by 2008
- 2006: EPA PFOA Stewardship Program
  - Remaining 8 major manufacturing companies committed to reduce PFOA and other longer chain PFCAs by 2015
- Replacement technologies
  - Reformulation
  - Shorter chain PFAS
  - Information is limited
  - Most not detected by standard methods
  - Treatment may not be as effective as for longer chains

PFAS Overview

- Overview
  - Chemistry
  - Environmental Concerns
  - Characteristics and Usage
- Fate and Transport
- Toxicology

PFOA & PFOS

- Most extensively produced and studied PFAS
- PFOA (perfluorooctanoic acid)
  - DuPont primary manufacturer
  - Teflon, Stainmaster, Scotchguard
  - Voluntary phase-out in 2006
- PFOS (perfluorooctane sulfonate)
  - 3M primary manufacturer
  - Aqueous Film Forming Foam
  - Voluntary phase-out between 2000 & 2002

C8 compounds
PFOS-based AFFF is used to extinguish flammable liquid fires often found near fire-training areas.
Other releases: PFAS production/manufacturing facilities, tank and supply line leaks.

GenX

- Used in the manufacturing process for high-performance polymers:
  - Cables
  - Non-stick coatings for cookware
  - Laptops
  - Cell phones
- Introduced by DuPont in 2008/2009 to replace PFOA

C6
In 2008, EPA received chemical notices under TSCA for two GenX substances: HFPO and HFPO ammonium salt
HFPO = Hexafluoropropylene oxide dimer acid

PFAS Properties

- Man-made compounds
- Repel water and lipids
- Stable, fully fluorinated carbons
- Resist environmental degradation
- Very low volatility
- Water soluble → migration from soil to gw → distant transport

Highly persistent in the environment.
Ultimate fate: sw

Human Routes of Exposure

- Ingestion of contaminated water and food
  - Ground water contamination due to spills and fire-fighting applications
  - Significant bioaccumulation in fish
  - Crops: uptake in some root vegetables, aerial deposition on crop surfaces
  - Food stored in PFAS-containing packaging
- Inhalation of airborne particulate
- PFAS half-life in humans: 2 to 9 years

PFAS-containing particulate quickly settles to the ground.
Volatility is low.
Studies in animals indicate that dermal toxicity is low.
Half-life = the amount of time it takes for the concentration of a chemical to decline by ½ through biological elimination processes.
PFOA = 2 – 4 yrs; PFOS = 5 – 6 yrs; GenX = unknown, but probably less than PFOA/PFOS due to shorter chain, but persistence and toxicity is probably similar.

PFOA Toxicity

- Probable link to carcinogenicity in humans
  - Kidney
  - Testicular
- Probable link to non-cancer effects in humans
  - High cholesterol
  - Ulcerative colitis
  - Thyroid disease
  - Pregnancy-induced hypertension

C8 Study: releases of PFOA in Parkersburg, WV (Washington Works Plant) from the 1950s to the early 2000s.
Exposure and health studies conducted 2005 – 2013.
Interviews, questionnaires, and blood samples collected from 69,000 people living near the plant. Findings presented in slide.
Resulted in $670 million settlement by DuPont to impacted individuals.

PFOS Toxicity

- Suggestive evidence of carcinogenicity in rats
  - liver, thyroid, mammary
- Non-cancer critical effects in lab animals
  - Reproductive & developmental effects, liver & kidney toxicity, immune suppression
- Non-cancer findings in humans
  - High cholesterol, low birth weight, immune suppression, thyroid hormone disruption

GenX Toxicity

- Limited data, derived solely from experimental studies in lab animals
  - Tumors in pancreas, liver, & testes
  - Kidney & liver disease/degeneration
  - Reproductive effects: uterine polyps, early birth, lower fetal weight, fetal skeleton deformation, delayed puberty

High-dose exposures to lab animals in an effort to extrapolate potential toxicity in humans.

PFAS Ecological Toxicity

- Acknowledgement
  - Eco slides were created by **Kimberly Plank**, Ph.D., of R3's Biological Technical Assistance Group (BTAG).
- Disclaimer
  - I condensed Kimberly's slides for this presentation and take full responsibility for any butchering that occurred in the transition.

Ecological Routes of Exposure

Receptor Category	Media	Exposure Route
Plants	Soil, sediment, water	Root Uptake
Insects	Soil, sediment, water	Direct Uptake
Other Invertebrates	Soil, sediment, water	Direct Uptake
Fish	Water	Direct Uptake
Amphibians	Water, sediment, soil	Direct Uptake
Reptiles	Soil, water	Diet/Incidental Ingestion
Birds	Soil, sediment, water	Diet/Incidental Ingestion
Mammals	Soil, water	Diet/Incidental Ingestion

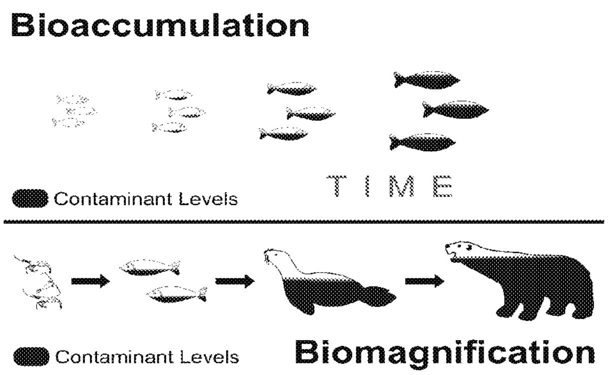
- Receptors include plants (terrestrial & aquatic) and animals (terrestrial, & aquatic), including insects.

PFAS Ecological Concerns & Toxicity

- Readily bioavailable
- Bioaccumulate & biomagnify*
- Cause detrimental effects
- Relevant tox endpoints:
  - Reproduction
  - Growth
  - Mortality

*Simple, but excellent graphic in next slide.
Eco receptors should be considered in PFAS risk assessments.

Bioaccumulation & Biomagnification



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PFAS Triggers / Clean-Up Goals

- Lifetime Health Advisory
  - 70 ppt for PFOA/PFOS in public drinking supplies
  - Developed by EPA's Office of Water (May 2016)
- Other (sometimes lower) values are out there
  - State-promulgated levels for drinking water
  - ATSDR risk levels for PFOA & PFOS

1 ppt is equivalent to three seconds out of every hundred thousand years.
Values differ due to differences in interpreting critical tox studies, exposure considerations, level of tolerable risk, etc.

PFAS Issues

- Highly desirable commercial applications
- Sample collection & analyses
  - To avoid cross-contamination, collection & analyses requirements are stringent
  - Not many labs are set-up to perform PFAS analyses → lab shortage, long wait times
  - Lack of analytical and data validation protocols for media other than drinking water

PFAS compounds are very effective at resisting water, grease, and stains.

PFAS Issues
(cont.)

- Water treatment
  - Limited options available (GAC)
  - Treatment to remove PFOA/PFOS appears to be ineffective for GenX
- There are so many PFAS that we know nothing about

Treatment to remove PFOA/PFOS appears to be ineffective for GenX.

Path Forward

- ORD evaluating toxicity of other PFAS
- Improving analytical methods and scope
- Developing multi-lab validation methods
- EPA PFAS Management Plan
  - Begin MCL process for PFOA & PFOS
  - Haz substance designation for PFOA & PFOS
  - Enforcement, monitoring, research, and risk communication

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